

NO-A175 656

ISOTHERMAL VAPOR PHASE EPITAXY OF MERCURY CADMIUM
TELLURIDE(U) STANFORD UNIV CA DEPT OF MATERIALS SCIENCE
AND ENGINEERING J G FLEMING ET AL. 1986

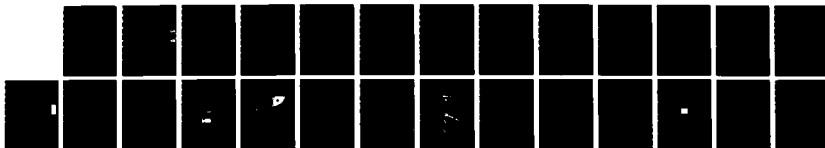
1/1

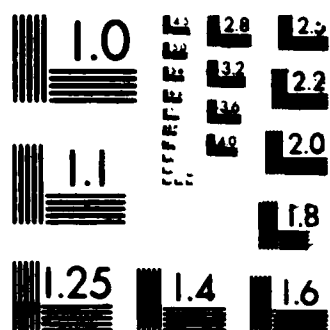
UNCLASSIFIED

N00014-84-K-0423

F/G 20/12

NL





AD-A175 656

OTIC FILE COPY

ISOTHERMAL VAPOR PHASE EPITAXY OF MERCURY CADMIUM TELLURIDE

J. G. Fleming and D.A. Stevenson.

Materials Science and Engineering Department,

Stanford University, Stanford CA. 94305.

1986

N00014-84-K-0423

A model is presented for the thermodynamic and kinetic basis of isothermal vapor phase epitaxy (ISOVPE) of mercury cadmium telluride. Growth is the result of a combination of transport of Te_2 and Hg from the source to the substrate and interdiffusion between Hg and Cd in the growing layer. Using a Te-rich mercury cadmium telluride source, it is possible to fix the surface composition of the growing layer. The observed effects of time, source to substrate spacing, temperature, and mercury overpressure are explained using the model.

1. Introduction

Mercury cadmium telluride ($\text{Hg}_{1-x}\text{Cd}_x\text{Te}$) epilayers are of great interest for use in infrared detectors. Isothermal vapor phase epitaxy (ISOVPE) of this material has been studied since the 1960's [1-15]. The technique has a number of advantages: simplicity, good surface quality, and ease of scale up. One disadvantage is that it produces only graded junctions. Although many growth trends have been reported in the literature, the relevant pressure-temperature diagrams and basic thermodynamic data for the HgTe-CdTe solid solutions have only recently been determined [16-18]. This information is essential to an understanding of the growth process. The objective of the present study is to confirm and supplement the existing information on the growth kinetics and to analyze the process in terms of thermodynamic driving forces and kinetic

SELECTED
JAN 05 1987

86 5054

This document has been approved
for release and sale; its
distribution is unlimited.

37

1 2

037

models in the light of this information. A better understanding of the growth mechanism should provide a basis for improving the growth technique and lend insight into the properties of the material itself.

A major problem in analyzing the mechanism of growth is the large number of variables involved. These include: growth temperature, mercury overpressure, source composition, substrate orientation, source to substrate spacing, and the growth time. To simplify the problem, we have investigated one variable at a time while keeping the others fixed. An analysis of our results and those in the literature has enabled us to develop a theory which qualitatively explains the observed trends of this growth process.

2. Experimental.

The general growth geometry is shown in fig.1. A relatively large source-to-substrate spacing was used since previous workers had shown that growth is a strong function of spacing for small spacings [1,15]. A large spacing minimizes variations due to slightly different spacings. The {111} CdTe substrates were etched for 30 seconds in a 4% bromine-methanol solution just prior to growth.

Our source consisted of a mixture of solid mercury cadmium telluride of a given fraction CdTe (including pure HgTe) and an equilibrium Te-rich liquid with a ratio of solid to liquid ~9/1. The liquid composition was taken from the LPE melt compositions reported by Harman [19]. Thus, at the growth temperature, this source consists of three phases: solid, liquid and vapor. Large amounts of source were made up by annealing the elements at 650°C



<input checked="checked" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	
<i>the on file</i>	
Codes	
1/ or	
Dist	Special
A-1	

for 16 hours, quenching the ampoule in water, and powdering and sintering the resulting material at 500°C for 30 minutes to ensure homogeneity. The amount of source used per growth was ~1-1.5 grams.

After growth, the cross section composition profiles were determined using electron probe microanalysis by suitably mounting, sectioning, polishing, and coating the samples. In some experiments, the position of the original substrate surface was established by alumina markers placed on the surface by dipping the substrates into a slurry of 0.3 micron diameter alumina particles in acetone and then air drying the surface. After growth, this produces a fine line of particles and defects which can be highlighted by a 30 second Polisar 2 etch.

3. The Thermodynamic Driving Force.

Figure 2 gives a composition versus distance plot with the position of the original substrate surface indicated and clearly shows that material has been added to the CdTe substrate. The metal to non-metal ratio is maintained throughout the solid, indicating that deposition occurs stoichiometrically. Even though the process is isothermal, there is a chemical gradient driving force for this deposition. Tung et al. [17], in their paper on the pressure-temperature diagrams of mercury cadmium telluride, present values for the entropy and enthalpy of CdTe and HgTe in the solid solution. The calculated free energies of HgTe, ($G_{\text{HgTe}} = H_{\text{HgTe}} - TS_{\text{HgTe}}$) and CdTe at 550°C versus X (where X is the fraction of CdTe in $\text{Hg}_{1-X}\text{Cd}_X\text{Te}$) are given in figs. 3 and 4. These graphs show that the

total free energy of the system decreases upon alloying HgTe-rich and CdTe-rich material, as expected for stable solid solutions. This is the thermodynamic driving force for isothermal vapor phase growth. However, this does not provide information on the kinetics or mechanism of the growth process, which are of major practical interest.

4. The source of Cd.

A key question in the growth mechanism is the source and transport mechanism of the Cd in the growing MCT layers; does the Cd come from the source or the substrate or both? We propose that all the Cd in the layer comes from the substrate by Hg and Cd interdiffusion. Area B of fig. 2 corresponds to the amount of Cd transported from the substrate and is roughly equal to area A, which corresponds to the amount of Cd present in the HgCdTe outside the original substrate surface. (These areas are directly proportional to the amount of Cd since the lattice parameter of MCT solid solutions changes only slightly with composition.) A further analysis of 27 samples grown under a variety of conditions shows that, on the average, area B is 15% larger than area A. This discrepancy is at least partially due to a systematic error in the microprobe profiles which occurs in the region where the profiles are changing rapidly. The error arises from the finite beam size, and beam spreading within the sample which effectively increases the layer transition region, thereby increasing area B. Another possible reason is a Kirkendall effect moving the alumina markers away from the position of the original CdTe surface towards the vapor-solid

interface. The Kirkendall effect in this system was reported by Leute and Stratmann [20]. Furthermore, the partial pressure of Cd in the system is very low [16,17] and the transport of Cd from the substrate to the source is expected to be small; thus, to a good approximation, we may consider the growth as consisting of vapor transport of HgTe only, with interdiffusion taking place between CdTe and HgTe to form the HgCdTe layer.

5. HgTe Transport.

Insight into the transport of HgTe is provided by the pressure-temperature diagrams of this system [17]. These are given in fig. 5 and show that, at all temperatures and compositions, the partial pressure of Hg is dominant. Since the mercury partial pressure is so large, it should be unaffected by the relatively slow growth process and remain constant throughout the ampoule. Svob et al. in their study of the growth process [14,15] maintain that the mercury pressure in the growth system changes with time. However, the sources used in their studies, HgTe annealed to Hg-rich conditions with added free Hg, were different than ours. In accord with the Gibbs phase rule, the three phase equilibrium source used in the present study provides constant component partial pressures over the source at a constant temperature and a fixed composition of solid in the source. The overall composition of the source is not appreciably altered since the source is very much larger than the layer grown. Furthermore, the amount of change in the mercury partial pressure, reported by Svob et al [14,15] to be due to vacancy

formation, is in disagreement with studies on the width of stability of the mercury cadmium telluride system. [21]

Because the Te_2 pressure is much smaller than the Hg pressure, Te_2 transport from source to substrate is expected to be rate limiting, at least in the early stages of growth. Figure 6 shows the variation in the Te_2 partial pressure with fraction CdTe in the mercury cadmium telluride for the conditions of growth: constant growth temperature and Hg pressure. This graph indicates that there is a gradient in Te_2 partial pressure between the source and the substrate; during growth, Te_2 vapor is transported down this partial pressure gradient from the HgTe-rich source to substrate surface where it supersaturates the vapor and deposits HgTe. Figure 6 also establishes that it is not possible to grow material with a lower fraction CdTe than the source since this would require Te transport up a partial pressure gradient. Another view of the driving force is provided by noting that the mercury vapor pressure is fixed by the three phase Te-rich source and in, accord with the Hg-Cd-Te pressure-temperature diagram (Fig. 5), material with higher HgTe fractions is not stable in this environment and therefore can not form.

6. The Effect of Source Composition.

The source consists of a solid-liquid-vapor mixture in equilibrium with the desired MCT composition. Further details of this type of source are described elsewhere [22]. The source was prepared by mixing solid HgCdTe of the desired composition with its equilibrium Te-rich liquid in a 9/1 molar ratio. At temperature, the

solid-liquid mixture vaporizes to supply the third phase. As has already been mentioned, in accord with the Gibbs Phase Rule for a three component system such as HgCdTe, three phases will correspond to two degrees of freedom. Thus, specifying the temperature and the solid composition will fix all of the intensive properties of the system. In practice the solid composition of the source is fixed as long as the amount of HgTe deposited is small with respect to the amount of HgTe in the source.

Both Becla et al [8] and Kay [11] have reported that the layer surface composition and thickness depend on the fraction of Te-rich melt in the source. This should not be the case from purely thermodynamic considerations. However, these two authors report different findings; in one case the surface CdTe fraction reportedly increases with increasing Te fraction [8], while the opposite trend is reported for the other study [11]. Purely thermodynamic arguments may not apply for the initial stages of growth when the source and substrate surface are well displaced from equilibrium, but should apply for the stages of growth when the growing layer surface composition is close to the source composition. In this analysis we will only consider this near equilibrium condition.

7. The Effect of Growth Time.

Figure 6 illustrates that there is a gradient in the Te_2 partial pressure favoring transport as long as the fraction of CdTe in the source is less than that at the growing surface. As growth proceeds, interdiffusion between Hg and Cd maintains this gradient. Figure 7 shows a plot of the log of the amount of HgTe transported versus log

time. Initially, the layers are thin enough that Cd and Hg can quickly interdiffuse and growth is limited by transport of Te_2 from the source to the substrate. This vapor transport limitation gives rise to the initial linear portion of the curve. This initial linear dependence has been observed in the literature [5,11,12]. For longer times, the layer thickens and growth is limited by interdiffusion of Cd and Hg increasing the fraction of CdTe at the growing surface. In this regime, growth follows the $t^{1/2}$ dependence expected for a diffusion limited process; this $t^{1/2}$ dependence has been observed in other studies [1-8,12-15]. As the thickness of the growing layer increases, the composition of the surface approaches that of the source. Eventually, growth is purely diffusion limited and the surface composition becomes essentially the same as that of the source.

8. The Effect of Temperature.

Figure 8 shows the effect of changing the growth temperature while keeping all other variables fixed. As the growth temperature is lowered, the surface composition approaches that of the source and the layers are thinner. The observed interdiffusion activation energy is ~ 2 eV [23,24]. The activation energy governing the Te_2 partial pressure under Te-rich conditions can be deduced from the equation given by Schwartz et al and is on the order of 1.2 eV [16]. Thus, growth will be strongly temperature dependant, with the interdiffusion process being primarily effected. Lowering the temperature produces thinner layers with lower surface fractions of

CdTe which is consistent with a relatively lower interdiffusion rate as compared to the HgTe vapor transport rate.

9. The Effect of the Substrate Polarity and Source to Substrate Spacing.

The effect of CdTe {111} surface polarity was addressed for this process by simultaneously depositing on both the A and B faces. This was achieved by orientating the substrate as shown in fig. 9. To within experimental error, no effect on either surface composition or thickness was observed. This is expected since these experiments were performed in the diffusion limited regime and interdiffusion will be unaffected by the surface polarity. However, there may be an effect at shorter times when growth is transport limited. The surface morphology of the layers was found to vary between the A and B faces. While both surfaces were macroscopically smooth, the A face had a more pronounced microscopic surface terrace structure.

The same experimental geometry was also used to determine the influence of source to substrate spacing and the results are given in fig.10. Similar trends on the effect of source to substrate spacing were reported by Svob et al. [15] from a study of separate growth runs. From the present study, we see that increasing the source to substrate spacing increases the surface CdTe fraction and decreases the layer thickness. An explanation of this behavior is that as the source to substrate spacing increases, the flux of Te₂ should decrease since the Te₂ potential gradient will decrease, reducing the amount of HgTe deposited. This experiment is complicated by the possibility of Te₂ depletion resulting from

deposition occurring on parts of the substrate which are closer to the source. However, the fact that there is an observable dependence on distance from the source is evidence that growth is, at least initially, limited by transport of Te_2 and not a surface reaction of Hg and Te_2 at the growing surface or interdiffusion, neither of which depend on spacing.

10. The Effect of Mercury Overpressure.

Becla [9], Svob [15] and Tufte [4] have investigated the effect of the ambient pressure of Hg on the surface composition grown. In these studies the Hg partial pressure was controlled by either a two zone technique [9] or by adding a fixed amount of Hg to the growth ampoule [4,15]. This work has shown that increasing the mercury partial pressure results in layers which are thinner and have higher surface fractions of CdTe. Increasing the partial pressure of the Hg will have several effects on growth. The partial pressure of Te_2 over both the source and the substrate will decrease in accord with the equilibrium constant, $P_{\text{Te}_2} = K/(P_{\text{Hg}})^2$. The mobility of the Te_2 in the vapor will also decrease inversely as the total pressure increases. Both these effects would give rise to the higher CdTe fractions and thinner layers observed at higher Hg pressures. The Hg pressure might influence the interdiffusion coefficient, although, previous studies [20] have shown that interdiffusion is relatively insensitive to this parameter. Furthermore, if the dominant effect of increasing the mercury overpressure was to lower the interdiffusion coefficient, then the surface composition of the

layers should approach that of the source, while the opposite is the case .

Another effect comes into play when the mercury pressure falls below the minimum value for which HgTe is stable. In this case only more CdTe rich material will be stable. The minimum mercury partial pressure for which mercury cadmium telluride of a certain composition is stable is given by the pressure-temperature diagrams for the system. By accurate control of the mercury partial pressure, for example using a two zone system, it is possible to set a lower limit of CdTe at the surface of the layer. This effect has been observed in the work of Becla [9].

11. Summary.

Isothermal vapor phase growth is the result of two processes: transport of Te_2 and Hg (though only the transport of Te_2 is limiting) from source to substrate and interdiffusion between Hg and Cd within the growing layer. At short times, growth is limited by the transport of Te_2 while at longer times growth is diffusion limited. Eventually, growth becomes entirely diffusion limited and the surface composition becomes essentially equal to that of the source. The time it takes for this to occur is greater for material with lower CdTe fractions, higher temperatures, higher mercury overpressures and greater source to substrate spacings. Increasing the Hg overpressure decreases both the partial pressure and the mobility of Te_2 vapor. If the mercury overpressure is sufficiently low, then the lower limit of the CdTe fraction in the layer is

determined by the materials' lower limit of mercury partial pressure stability.

Acknowledgements:

The authors thank Drs. R. Kay and K. Zanio of Ford Aerospace for helpful discussions and Dr. Margaret Brown of Rockwell International for helpful discussions and for supplying CdTe substrates. One of the authors, J. G. Fleming, gratefully acknowledges the support of an ONR fellowship. This work was funded by DARPA through the Office of Naval Research, contract no. N00014-84K-0423.

References.

- [1] G. Cohen-Solal, Y. Marfaing, F. Bailly and M. Robot, C.R. Acad. Sc. Paris. 261 (1965) 931.
- [2] Y. Marfaing, G. Cohen-Solal and F. Bailly, J. Phys. Chem. Sol. Suppl. 1 (1967) 549.
- [3] G.S. Almasi and A.C. Smith, J. Appl. Phys. 39 (1968) 233.
- [4] O.N. Tufte and E.L. Stelzer, J. Appl. Phys. 40 (1969) 4559.
- [5] L. A. Bovina, V.P. Meshcheryakova, V.I. Stafeev and E. S. Banin, Soviet Physics-Semiconductors. 7 (1973) 26.
- [6] J. M. Pawlikowski and P. Becla, Phys. Stat. Sol. (a) 32 (1975) 639.
- [7] J. M. Pawlikowski, Thin Solid Films, 44 (1977) 241.
- [8] P. Becla, J. Lagowski, H. C. Gatos and H. Ruda, J. Electrochem. Soc. 128 (1981) 1171.
- [9] P. Becla, J. Lagowski, H. C. Gatos and L. Jedral, J. Electrochem. Soc. 129 (1982) 2855.
- [10] P. Becla, J. Lagowski and H. C. Gatos, J. Electrochem. Soc. 129 (1982) 1103.
- [11] R. E. Kay, U.S. Patent #4,447,470 May 8 1984.
- [12] Y. Nemirovsky and A. Kepten, J. Electronic Materials 13 (1984) 867.
- [13] P. Becla, P. A. Wolff, R. L. Aggarawal and Y. S. Yuen, J. Vac. Sci. Technol. A 3(1) (1985) 119.
- [14] F. Bailly, L. Svob, G. Cohen-Solal and R. Triboulet, J. Appl. Phys. 46 (1975) 4244.
- [15] L. Svob, Y. Marfaing, R. Triboulet, F. Bailly and G. Cohen-Solal, J. Appl. Phys. 46 (1975) 4251.
- [16] J. P. Schwartz, T. Tung and R. F. Brebrick, J. Electrochem. Soc. 128 (1981) 438.
- [17] T. Tung, L. Golonka and R. F. Brebrick, J. Electrochem. Soc. 128 (1981) 451.
- [18] C.-H. Su, P.-K. Liao and R. F. Brebrick, J. Electrochem. Soc. 132 (1985) 942.
- [19] T. C. Harman, J. Electronic Materials. 9 (1980) 945.
- [20] V. Leute and W. Stratmann, Z. Physik Chem. 90 (1974) 172.
- [21] H. F. Schaaake, J. Electronic Materials, 14 (1985) 513.
- [22] J.G.Fleming and D.A.Stevenson, Submitted for publication.
- [23] J.G.Fleming and D.A.Stevenson, Submitted for publication.
- [24] K.Zanio and T.Massopust, J. Electronic Materials, 15 (1986) 103.

Fig. 1. The experimental geometry used throughout this work. Before growth, and immediately after the substrates were etched, the ampoules were evacuated to $\sim 10^{-5}$ torr and sealed.

Fig. 2. A plot of a typical composition profile. The growth time was 16 hours at a temperature of 550°C , and the source was in equilibrium with Te-rich $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$. The position of the original substrate surface, observed by alumina markers placed on the surface before growth is also shown. Area A is approximately equal to area B, which is directly proportional to the amount of Cd which has "diffused" (interdiffused with Hg) out of the substrate; indicating that the cadmium in the film originates from the CdTe substrate.

Fig. 3. The free energy of formation of HgTe in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ versus composition at 550°C . The relevant data are taken from Tung et al. [17]

Fig. 4. The free energy of formation of CdTe in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ versus composition at 550°C . The relevant data are taken from Tung et al. [17]

Fig. 5. The pressure-temperature diagrams for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ determined by Tung et al. [17] Closed and open symbols represent experimental and calculated values respectively. Since the material is a ternary, each composition exists over a different range of partial pressures. $\blacktriangle, \triangle$ for $X=0$; \bullet, \circ for $X=0.094$ and $X=0.108$; \blacksquare, \square for $X=0.194$; $\blacktriangledown, \triangledown$ for $X=0.416$; and \blacklozenge, \lozenge for $X=0.581$.

Fig. 6. The variation of tellurium partial pressure with composition for the conditions of isothermal vapor phase growth, constant temperature and mercury pressure. A temperature of 550°C and mercury pressure of 1 atm. are used as a example. The tellurium partial pressure was determined from the entropy and enthalpy data given by Tung et al. [17]

Fig. 7. A plot of the log of the amount of HgTe transported versus log time (hours) for samples grown at 550°C from a Te-rich HgTe source. As time increases, growth becomes diffusion limited as evidenced by the 1/2 slope.

Fig. 8. The effect of growth temperature on layers grown from Te-rich HgTe for a time of 24 hours. As the temperature is increased, the interdiffusion coefficient increases, leading to thicker layers with higher surface X values.

Fig. 9. The experimental geometry used to investigate the effect of the source to substrate spacing and {111} substrate polarity on growth. The substrate is oriented vertically with respect to the source so that different points on the substrate are different distances from the source and the A (Cd) and B (Te) faces are both exposed to the same environment.

Fig. 10. The effect of source to substrate spacing (horizontal axis) on layer thickness (left hand side vertical axis) and surface composition (right hand side vertical axis). The source used was Te-rich HgTe, the temperature was 550°C and the growth time, 16 hours.

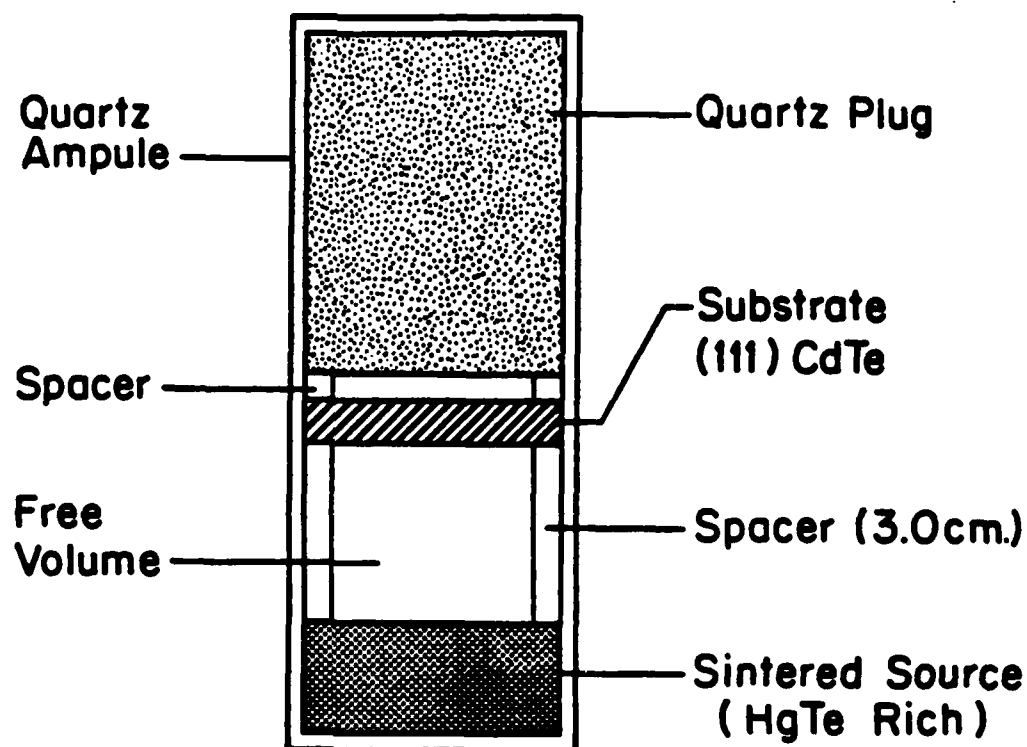


Fig. 1. The experimental geometry used throughout this work. Before growth, and immediately after the substrates were etched, the ampoules were evacuated to $\sim 10^{-5}$ torr and sealed.

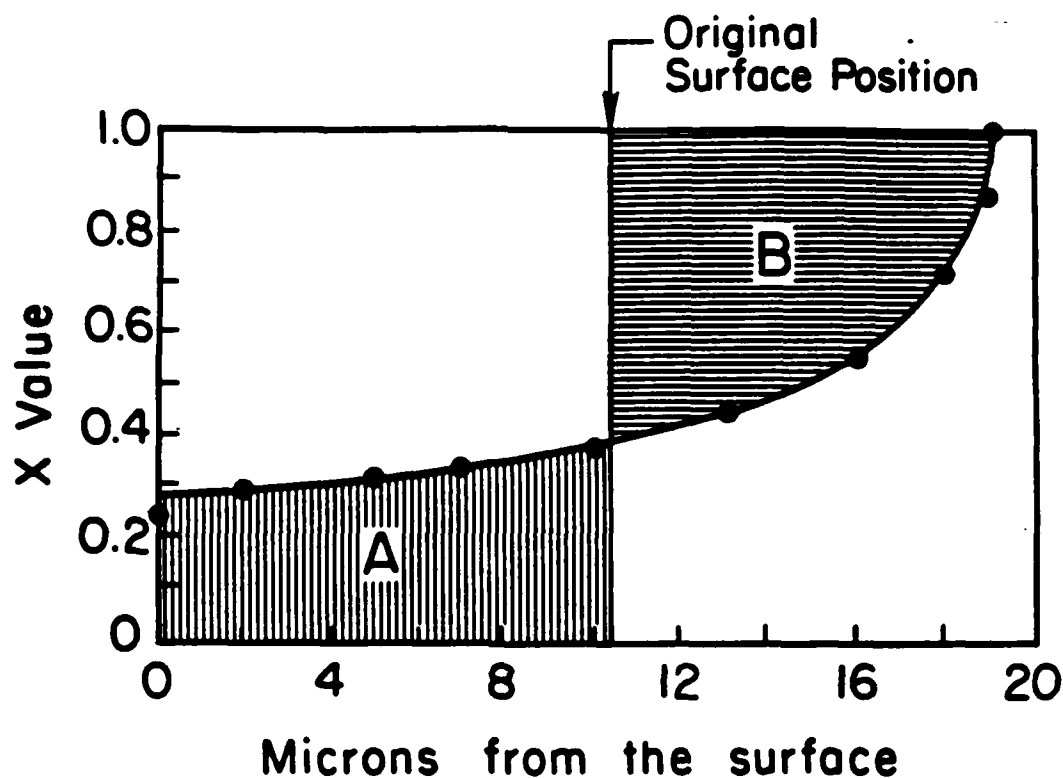


Fig. 2. A plot of a typical composition profile. The growth time was 16 hours at a temperature of 550°C, and the source was in equilibrium with Te-rich $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$. The position of the original substrate surface, observed by alumina markers placed on the surface before growth is also shown. Area A is approximately equal to area B, which is directly proportional to the amount of Cd which has "diffused" (interdiffused with Hg) out of the substrate; indicating that the cadmium in the film originates from the CdTe substrate.

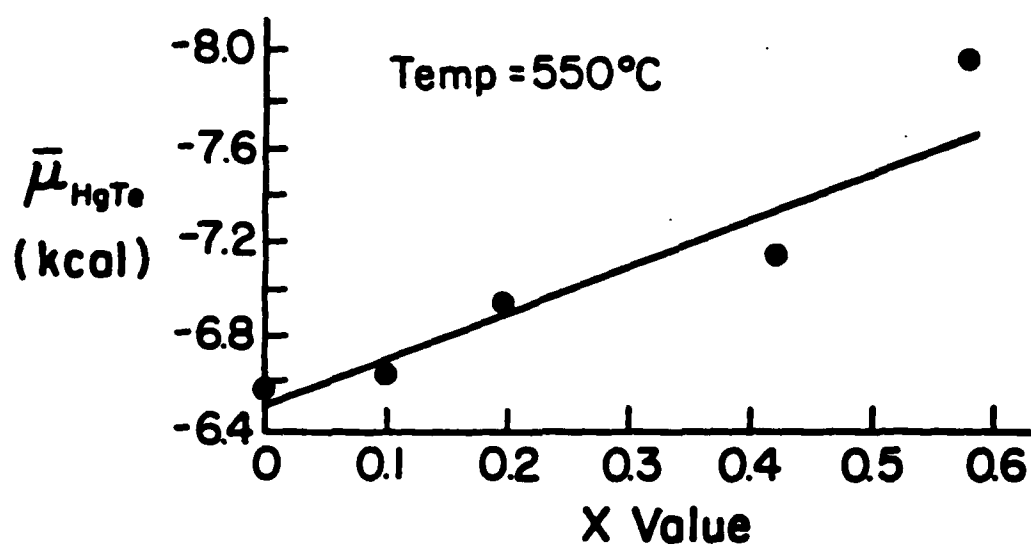


Fig. 3. The free energy of formation of HgTe in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ versus composition at 550°C . The relevant data are taken from Tung et al. [17]

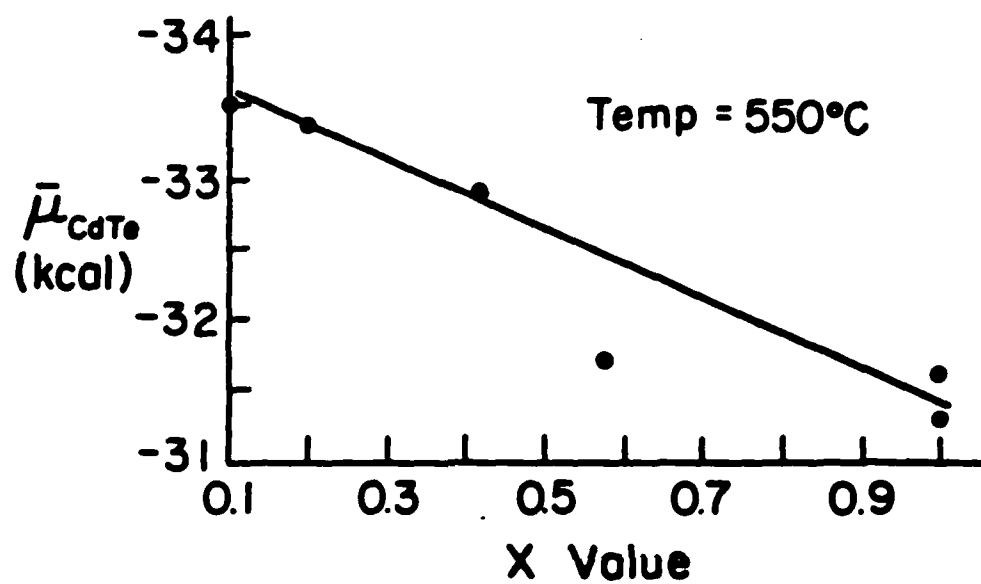
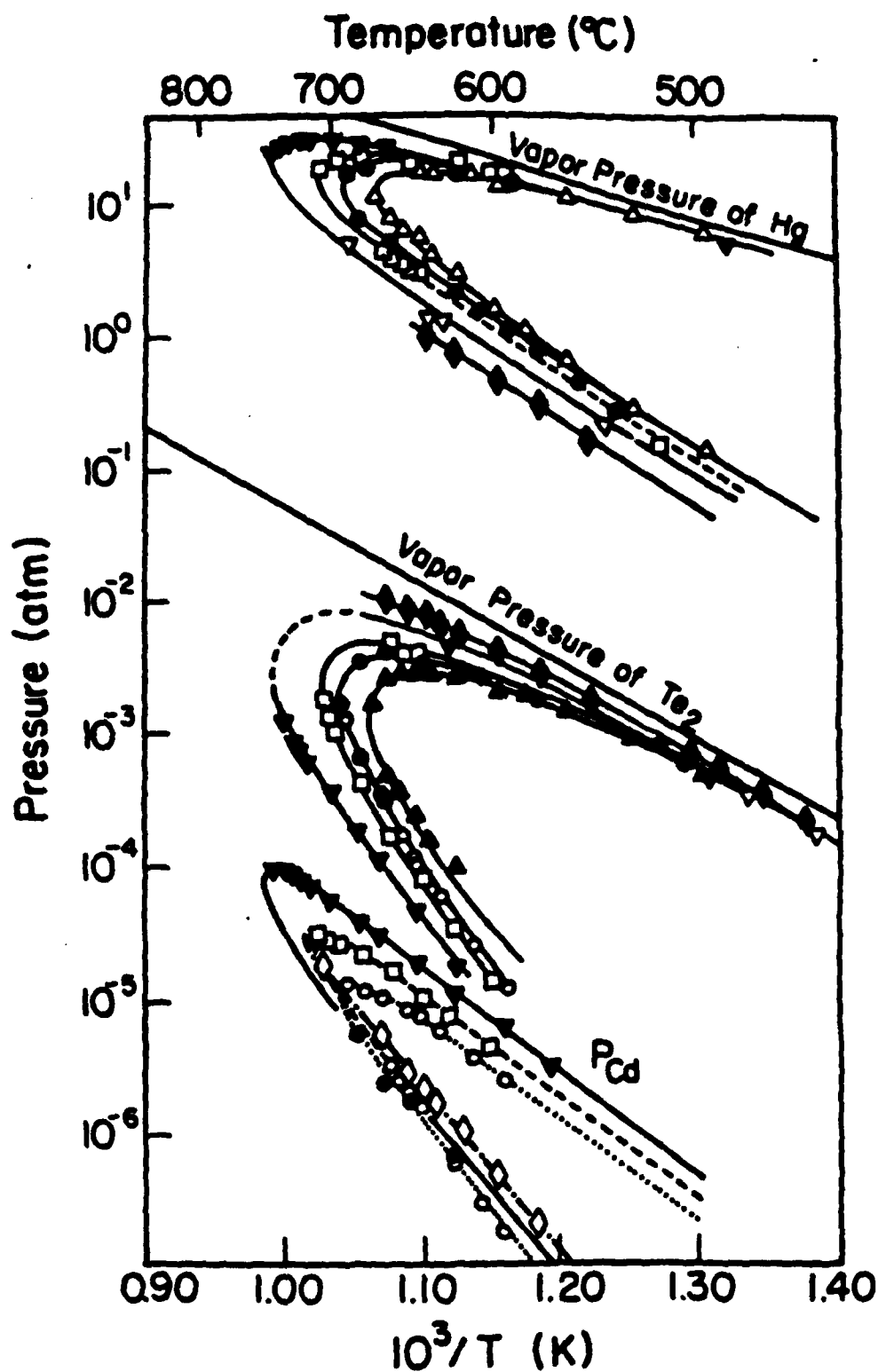


Fig. 4. The free energy of formation of CdTe in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ versus composition at 550°C . The relevant data are taken from Tung et al. [17]

Fig. 5. The pressure-temperature diagrams for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ determined by Tung et al. [16-18] Closed and open symbols represent experimental and calculated values respectively. Since the material is a ternary, each composition exists over a different range of partial pressures. $\blacktriangle, \triangle$ for $X=0$; \bullet, \circ for $X=0.094$ and $X=0.108$; \blacksquare, \square for $X=0.194$; $\blacktriangledown, \triangledown$ for $X=0.416$; and \blacklozenge, \lozenge for $X=0.581$.



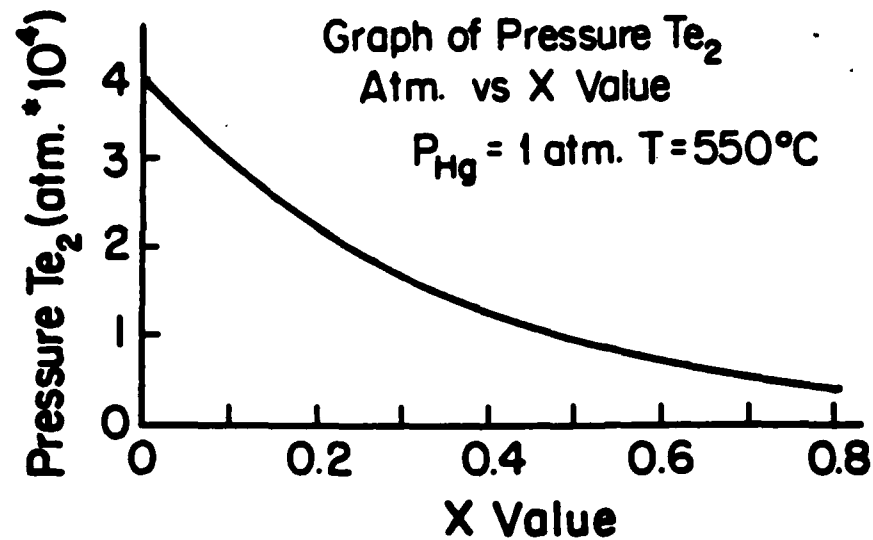


Fig. 6. The variation of tellurium partial pressure with composition for the conditions of isothermal vapor phase growth, constant temperature and mercury pressure. A temperature of 550°C and mercury pressure of 1 atm. are used as a example. The tellurium partial pressure was determined from the entropy and enthalpy data given by Tung et al. [17]

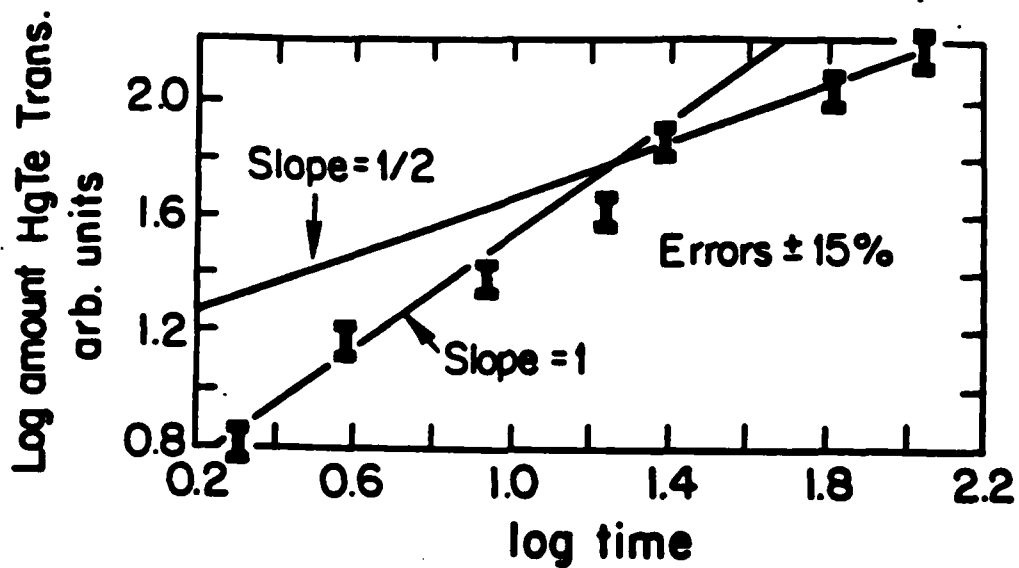


Fig. 7. A plot of the log of the amount of HgTe transported versus log time (hours) for samples grown at 550°C from a Te-rich HgTe source. As time increases, growth becomes diffusion limited as evidenced by the 1/2 slope.

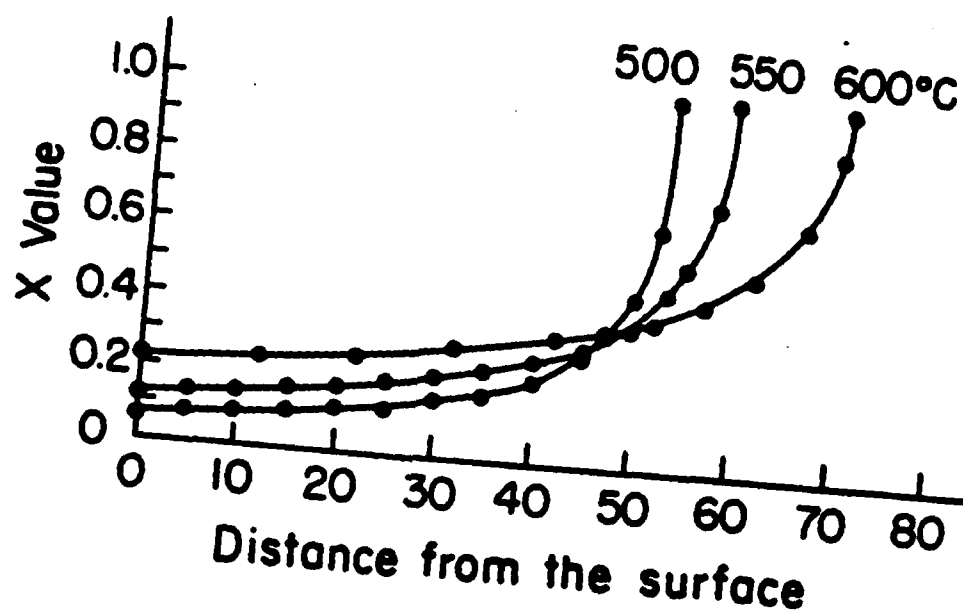


Fig. 8. The effect of growth temperature on layers grown from Te-rich HgTe for a time of 24 hours. As the temperature is increased, the interdiffusion coefficient increases, leading to thicker layers with higher surface X values.

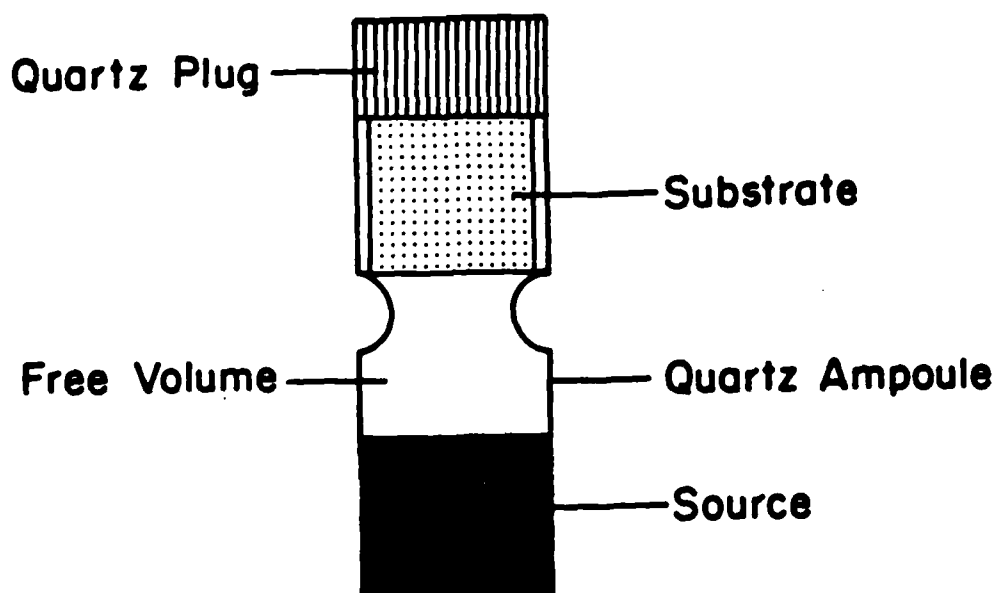


Fig. 9. The experimental geometry used to investigate the effect of the source to substrate spacing and $\{111\}$ substrate polarity on growth. The substrate is oriented vertically with respect to the source so that different points on the substrate are different distances from the source and the A (Cd) and B (Te) faces are both exposed to the same environment.

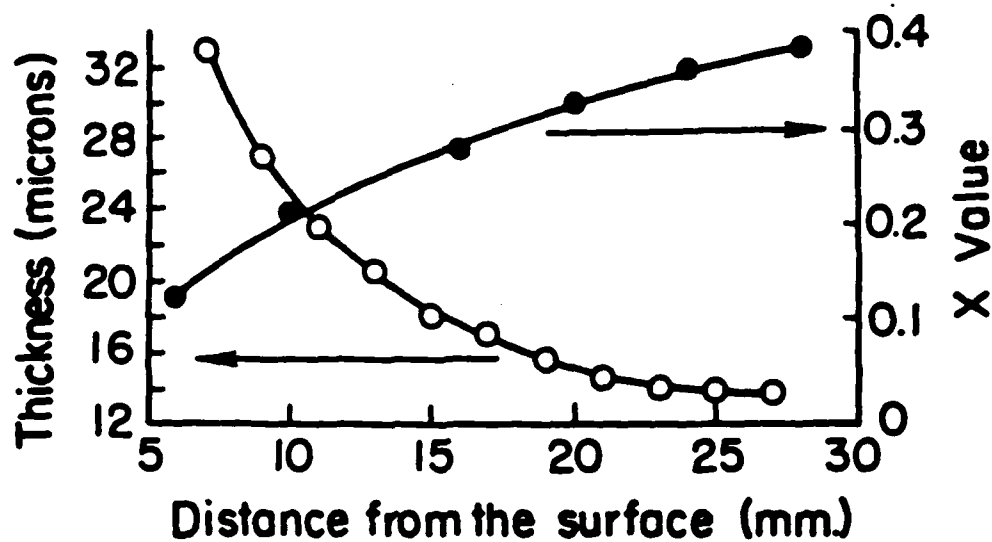


Fig. 10. The effect of source to substrate spacing (horizontal axis) on layer thickness (left hand side vertical axis) and surface composition (right hand side vertical axis). The source used was Te-rich HgTe, the temperature was 550°C and the growth time, 16 hours.

END

2-87-

DTIC